

TUNABLE INFRARED LASERS:  
PREPARING FOR EXPANDED USE IN ENVIRONMENTAL MONITORING

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The literature on the use of tunable infrared lasers for atmospheric trace gas detection and monitoring is about 25 years of age. However, this field, with its myriad of potential application areas, has always been driven by the available *laser* technology. As new or improved laser devices become available, with characteristics which lend themselves to operation in compact, nearly autonomous instruments, their application to atmospheric science and environmental measurements expands. We are now witnessing a period in which tunable infrared lasers are being used in well-engineered instruments on the ground, on emission stacks, in aircraft, balloon gondolas, and soon on Earth-orbiting spacecraft. The major **impact** of tunable lasers in remote sensing remains in the arena of sophisticated and expensive, one-of-a-kind instruments developed by technical groups in governments laboratories and universities. This will remain true in the near future. However, the steady progression of room temperature semiconductor diode lasers toward longer wavelengths in the infrared, and the burgeoning activity in OPO (Optical Parametric

Oscillator) laser technology, promise new tools for industrial monitoring and control applications as well as ambient air quality measurements.

### Basic Principles

Most gases and vapors have strong absorption bands in the infrared, with resonant frequencies (wavelengths) which depend on the vibrational characteristics of the bonds holding the atoms together. (The notable exceptions are nitrogen and oxygen, which are **homonuclear diatomic** molecules **with no** dipole moments.) These bonds undergo slight movements, in stretching or bending modes, in response to the electric field of light waves whose frequencies are near their natural resonances. The stretching modes of the light atoms tend toward high characteristic frequencies (short wavelengths) and the bending modes, especially with heavier atoms, occurring at the lower frequencies (longer infrared wavelengths).

The natural atmosphere itself contains certain infrared-active gases which absorb so strongly in regions of the infrared where their resonant absorption bands exist that these spectral regions are nearly opaque over path lengths of several meters to tens of meters. Figure 1 is a spectrum of atmospheric transmission for a path length of nearly 2 km. A spectrum such as this is instructive in pointing out the atmospheric **"window"** regions, which are highly desirable spectral regions for viewing the characteristic bands of trace gases or vapors. Favorite window regions for detection of

trace gases are the 3.4 - 4.1  $\mu\text{m}$  region and the 8 - 12  $\mu\text{m}$  region. If a similar spectrum of the atmosphere were taken through a vertical path extending through the entire atmosphere, the presence of the ozone absorption band in the 9.5  $\mu\text{m}$  region would be much more prominent, due to the stratospheric ozone.

Figure 1 is a low resolution spectrum, which does not show any detail within the molecular absorption bands. Actually there is a great deal of detail within the bands, because each vibration band consists of a large number of lines, due to the modulation of the vibration resonance by the rotations of the molecule. The molecular rotation causes periodic variation of the magnitude of the vibrating dipole moment with which the light wave can interact. The result is a splitting of the vibration resonance into a number of discrete vibration-rotation resonances. In the quantum mechanical picture there are many discrete quantum mechanical rotational energy levels for each vibration mode. With the simpler molecules consisting of two or three atoms, an absorption band appears as a comb spectrum, as in Figure 2 where a carbon dioxide band exists near the 2.05  $\mu\text{m}$  wavelength. With larger molecules the spectra appear to be quite complex, as with the nitric acid ( $\text{HNO}_3$ ) vapor example pictured in Figure 3. The spectra which appear in Figure 3 are taken with high resolution instruments, a large laboratory FTIR (Fourier Transform IR spectrometer) instrument, and a tunable diode laser spectrometer. (The wavenumber units which spectroscopists prefer to use are directly related to frequency, being the frequency divided by the speed of light. The inverse of

the **wavenumber** ( $\text{cm}^{-1}$ ) would be equivalent to the wavelength in vacuum in units of cm. ) Spectroscopists are able to model the line frequencies and strengths of such a complex spectrum as this with high accuracy using quantum mechanical calculations. Many of the larger molecules (e.g., vapors of the hydrocarbons which normally exist primarily as liquids) have such complex spectra that the vibration-rotation lines overlap and meld together at typical pressures and temperatures found in the lower atmosphere. In these cases, high resolution spectroscopy has no significant advantages in sensitivity or discrimination, and relatively gross features similar to the nitric acid band edge near  $1326 \text{ cm}^{-1}$  are used to identify the particular gas **or** vapor.

Spectroscopic techniques are 'not the only method for identification and measurement of gases and vapors in the air, but they have steadily increased in popularity over the past two decades. **Wet** chemistry and sophisticated gas **chromatographic** techniques would be considered the essential tools of analysis of air samples, due to the long history of technology and calibration methodology using these techniques, along with high specificity. For example, **chromatographic** techniques are unsurpassed in ability to separate and identify a wide variety of hydrocarbons. However these techniques require collecting and carefully handling samples. In many cases this is impractical or undesirable. Open path spectroscopic techniques can be used for remote sensing, for obtaining spatially averaged measurements, and for real time analysis. FTIR (Fourier Transform Infrared), gas correlation

spectrometers (which use absorption bands in the infrared) , and UV absorption spectrometers are the most utilized technologies for both global scale atmospheric monitoring and local environmental monitoring. (The Wspectroscopic detection relies on accessing absorption bands due to electronic transitions to upper energy levels, in contrast to the IR molecular vibration bands. The severe atmospheric absorption due to ozone and oxygen limits access in long path measurements to bands which exist in the "near-UV", i.e., near the blue wavelengths of the visible spectrum.) The FTIR and Wspectrometer instruments have gained popularity in recent years largely due to their **ability to** identify and quantify several constituents simultaneously.

The attraction of a laser source in the infrared for measurements of atmospheric gases is the large spectral radiance which can be obtained when compared with thermal or gas discharge sources of radiation. The detector/amplifier noise, combined with the absorption losses in the path between the source and the detector, often result in the desire for more available power from the source. The spectral widths **of** typical vibration-rotation absorption lines of gases or vapors near one atmosphere total pressure are near  $0.1 \text{ cm}^{-1}$ , or 3 GHz in frequency units. In the case of high resolution spectroscopic identification and measurement, when it is desired to resolve individual lines of a gas or vapor, the relevant question is how much usable power from the radiation source is available within this kind of spectral width. This is really a very small spectral width, approximately

$5 \times 10^{-5} \mu\text{m}$  at a wavelength of  $5\text{-}\mu\text{m}$ . A correspondingly small fraction of the power emitted from a broadband radiation source is available in such a small spectral interval. Comparing laser sources with the sun, we know that the sun, which is well described as a **blackbody** source at a temperature between 5000 X and 6000 K, can provide roughly  $10^{-10}$  watts of power per GHz in a diffraction limited spot or image at the detector of a spectral measurement instrument, in the wavelength region between 3-12  $\mu\text{m}$ . Thus even a low power semiconductor laser with e.g., 100  $\mu\text{W}$  available in a single **mode** (single frequency) , with spectral width much less than the gas absorption **linewidth**, beats the sun as a source by several orders of magnitude. Other thermal sources of IR radiation (e.g., **globars** or incandescent filaments) suffer even more in comparison.

The high degree of temporal coherence (spectral purity) and spatial coherence (near diffraction-limited output divergence) from the laser sources make them useful in a number of configurations. They can obviously be used in double-ended long path absorption spectroscopy measurements. They can be used successfully in multi-pass optical absorption cell arrangements, for real-time in-situ measurements. **Small cw** lasers can also be used as local oscillators in infrared heterodyne spectrometers, which are passive sensors (i.e. , not emitting laser radiation) used to detect trace gases. For these applications, a power level of the order of a milliwatt from a single mode laser is sufficient. Pulsed laser sources, normally with moderate to high output power, can be used as **lidar** transmitters. (**LIDAR** is actually an acronym for Light

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Detection and Ranging, similar to that for radar, which involves the use of a laser beam and usually range-gated detection electronics to probe the atmosphere.) Lidars are useful for truly long-range measurements, extending to ranges of kilometers or even several tens of km.

A sensitivity enhancing technique which can be used with lasers which continuously tune over a spectral range equivalent to at least several gas absorption linewidths is frequency modulation, combined with either harmonic detection or sideband detection. These techniques are capable of mitigating the effects of such nuisances as large DC offsets and baseline slopes when measuring very small **absorptances**. The frequency modulation of tunable diode lasers is commonly done by applying a small sinusoidal dither to a current ramp scan. The optimum sensitivity **is** obtained when the FM amplitude is approximately equal to the half-width of the gas absorption line **on** the frequency scale. Using these techniques, absorptances as small as one part in  $10^4$  can be measured with reasonably high accuracy.

The great advantage of lasers in spectroscopic **remote** sensing with their very high spectral radiance is offset to some extent by their relatively modest tuning ranges. For spectral survey applications, where a very wide spectral region is monitored in order to detect a large number of gases in one spectrum, a laser spectrometer cannot compete with an **FTIR** instrument in efficiency. Laser-based instruments are much better suited to applications for which one or more relatively narrow spectral regions are selected



for probing the volume of interest.

New laser technologies offer significant improvements in tuning capability, especially in the near infrared, with levels of reliability which represent significant progress . In the following sections we discuss several of the relatively new laser sources which are attractive for atmospheric sensing and environmental monitoring.

### Laser Sources

The development of new laser sources for atmospheric science and environmental monitoring is driven by the desire for use of efficient and convenient diode-laser pumping, eye safety considerations, and, as stated above, extended wavelength tunability.

Considerable progress has been made in Titanium-doped sapphire lasers (Ti:Sapphire) which can lase over a wide region of the near infrared, from 700 nm to 900 nm. These lasers can be optically pumped using frequency-doubled **Neodymium-doped YAG (Nd:YAG)** lasers, which in turn are pumped by compact arrays of diode lasers. These are the very mature compound semiconductor (gallium-aluminum arsenide) diode lasers with output wavelength near 800 nm, very similar to the mass-produced diode lasers' found in CD players. The **Nd:YAG** laser is mature and reliable, the garnet crystal being mechanically very strong, with a heritage of widespread military

applications. This wavelength region is useful for atmospheric water vapor measurements, which is the major objective of a new airborne instrument developed by NASA, and described in the next **section**. The Ti:Sapphire laser can be operated either in pulsed or **cw** modes. **It** is intrinsically a medium to high power laser, useful for long path measurements and single-ended measurements in which the signal is provided by **backscattering** from a topographic surface or from the atmospheric aerosol particles.

The tunable semiconductor **diode** laser itself has benefitted from several advancements in recent years, which should result in this laser technology becoming much more popular for environmental monitoring. When chemically composed of a variety of mixtures of elements, the semiconductor diode lasers can be made to **lase** in nearly any region of the infrared, out to 15  $\mu\text{m}$ . The exact chemical mix of elements dictates the energy bandgap of the active region and thus the operating wavelength of an individual diode laser, and the tunability is accomplished by varying the bulk temperature **or** the injection current passing through the active junction of the laser in a controlled fashion. Diode lasers have been used in high-tech environmental **monitoring** applications for two decades. The lead-salt diode lasers, which have been the only choice available until recently in the 2-15  $\mu\text{m}$  region, are now available with **mW** level single-frequency output power, each device tunable over several **wavenumbers**, with operating temperatures *in* the liquid nitrogen range.

An exciting recent development is the success in demonstrating

room temperature diode laser operation at longer wavelengths in the IR, using the III-V compound semiconductor materials and techniques for which a great deal of sophisticated device research is supported by the fiber communications industry. The use of quantum well structures provides narrower spectral output and **larger** tunability. Tunable diode lasers out to 2  $\mu\text{m}$  wavelength have been demonstrated using antimonide-based structures (**GaSb** substrates) and also **by** using strained-layer mixtures of **InGaAs** and **InGaAsP** on **InP** substrates. Output powers at the 1-watt level have recently been demonstrated near 2  $\mu\text{m}$ . There is considerable interest in pushing the operating wavelengths beyond 2  $\mu\text{m}$ , and the **antimonide-**based structures have the potential of **lasing** at wavelengths as long as 5  $\mu\text{m}$ . Although the fundamental absorption bands of most molecules of interest in environmental monitoring exist at wavelengths longer than 2  $\mu\text{m}$ , many have weaker overtone bands at wavelengths near or shorter than 2  $\mu\text{m}$ . In some cases, these bands are still strong enough for detection and monitoring of certain gases.

Another new laser source is the Optical Parametric Oscillator (**OPO**), or variations thereof. The heart of an OPO is a nonlinear crystal inside its own resonant cavity, which is pumped by an external laser. There is no population inversion in the crystal; it can **generate** coherent radiation through a nonlinear optical process which converts a beam of pump photons into two other beams of photons of lower momenta (longer wavelengths), called the signal and idler beams. Conservation of both energy and momentum in this

process dictate that only a certain combination of signal and idler wavelengths can be generated for a given crystal orientation and temperature. Wavelength tuning of either can be accomplished by either tuning the pump wavelength, or by careful mechanical rotation of the crystal, or by changing the crystal temperature. These devices can, with the right combination of laser pump wavelengths and nonlinear crystals, be made to operate at longer IR wavelengths than are available using the room temperature diode lasers. The potential of **OPO's** for environmental monitoring was recognized in the early **1970's**, but their actual use in field applications was extremely limited. Inadequate control of the output wavelength, the rather large spectral width of the output, and general reliability issues stifled interest. The recent renaissance in **OPO's** has been driven by the developments of **single-frequency** optical pumps (notably the diode-pumped solid-state lasers), and new nonlinear optical materials, such as **silver-gallium-selenide (AgGaSe<sub>2</sub>)**, which have opened up new wavelength ranges for atmospheric sensing. At present, several research groups have developed **OPO's** that operate in portions of the 3  $\mu\text{m}$  to 5  $\mu\text{m}$  range, and have moderate linewidths on the order of 0.1  $\text{cm}^{-1}$ . These **OPO's** are pumped by either **Erbium-doped** or **Holmium-doped** solid-state lasers, which emit near **2.8- $\mu\text{m}$**  and **2.0  $\mu\text{m}$** , respectively.

### Applications Areas

## Atmospheric Science and Global Environmental Concerns

Several instruments using tunable lasers have been developed and fielded for measurements of atmospheric chemical constituents which play important *roles* in the chemistry of the lower atmosphere (troposphere), and middle atmosphere (stratosphere and mesosphere) . These can generally be characterized as one-of-a-kind research instruments, developed largely by groups working at government laboratories or universities in the United States, Canada, Japan, and several European countries. A notable technique in this realm is the use of tunable laser transmitters in **lidars**. Tunable transmitters are often used in what is called **Differential-Absorption Lidar (DIAL)** systems, which tune on and off of absorption lines of gases of interest and depend on backscatter from the atmospheric molecules (**Rayleigh** scattering, mainly by nitrogen molecules) or the atmospheric aerosol particles to provide the return signals. Ratios of the logarithms of the signal returns vs. time, at the resonance and off-resonance wavelengths, result in profiles of the concentration of the gas or vapor along the line of sight. One of the most dramatic uses of a DIAL **system** is the airborne instrument employed by a group from the NASA Langley Research Center for studies of the ozone hole in the atmosphere above Antarctica and similar studies of the Arctic stratosphere (**Browell**, et al. ) . Other ground-based DIAL systems are being used in various locations, mainly in the Northern Hemisphere at **mid-latitudes**, to monitor the stratospheric ozone levels over long periods of time, to discern trends. Although these use near W

wavelengths, they are examples of techniques which can be applied to other atmospheric studies **using** tunable IR lasers as they are developed.

Two examples of recently developed instruments using tunable IR lasers are worth special mention because they are essentially autonomous airborne instruments. These instruments, both developed **by** NASA, represent results of considerable scientific and engineering experience which can be transferred to the general applications of lasers in the environmental monitoring fields. They have been engineered to fly on the NASA ER-2 high altitude aircraft, which requires autonomous operation except for periods when the investigators can service their instruments on the ground between flights.

The Aircraft Laser Infrared Absorption Spectrometer (ALIAS) is an instrument developed to measure several gases which are important in the stratospheric ozone chemistry, and it has been flown on arctic missions to study the mechanisms behind the ozone hole formation (Webster, et al. 1993). Figure 4 is a photograph of the instrument with the protruding sample inlet. It carries four lead-salt diode lasers and matching detectors in a single liquid nitrogen **dewar**, with each diode laser composition adjusted to **lase** in spectral regions corresponding to the bands of the molecules of interest. ALIAS is designed so that an ambient air flow inlet passes air samples through a multi-pass, 1-m length absorption cell. With the optics set up for 80 passes, some stratospheric species can be detected with mixing ratio sensitivities of tens-of-

parts-per-trillion. ALIAS is a product of several years of work by JPL scientists and engineers developing diode laser spectrometers for ground-based, balloon-borne, and aircraft measurement applications. The incorporation of new diode lasers which do not require cryogenic operating temperatures will take place as the laser technology progresses.

The LIDAR Atmospheric Sensing Experiment (**LASE**) instrument is a DIAL system developed by a NASA Langley Research Center group, employing a tunable Ti:Sapphire pulsed laser transmitter, which is pumped with a **Nd:YAG** laser. Figure 5 is a block diagram of the major functional units of the instrument. LASE will be flown beginning the early 1994, with the principal scientific goal being measurement of water vapor profiles over various locations of interest. It will also measure cloud distributions and elevated aerosol layers which may be present. The water vapor distributions are of course connected with cloud formation and dissipation, and water vapor itself plays a very important role as a greenhouse gas in the atmospheric radiation budget and the global warming interactions. This DIAL application demands high **spectral** purity from the transmitter, and this is achieved by injection-seeding the Ti:Sapphire cavity, **using** a tunable diode laser operating in the 800-820 **nm** region. LASE has the capability of probing several water vapor absorption lines of various line-strengths in order to cover the wide dynamic range of concentrations found in the atmosphere.

## Local Environmental Monitoring and Industrial Control

The use of tunable **IR** laser technology for measurements of pollutant gases affecting ambient air quality and gases associated with industrial process control **are** viewed as *emerging* applications. In order to make significant advances in these areas, the development of user-friendly laser sources in the atmospheric window regions is important. The 3.3-3.5  $\mu\text{m}$  region is rich with potential because of the **existence** there of the strong hydrocarbon C-H stretch band. The 8-12  $\mu\text{m}$  window region, often called the "**fingerprint**" region for the existence of a variety of bands which reflect the structure of the various gaseous hydrocarbons and organic vapors. Major impacts will be made with the development of robust, efficient **OPO's** in both of these spectral regions, and the development of compact TDLs at wavelengths as long as 4  $\mu\text{m}$ , which can operate at ambient temperatures, or possibly with small thermoelectric coolers.

As an example of such an application, Figure 6 depicts a schematic of a tunable diode laser sensor near 1.65  $\mu\text{m}$  wavelength (developed by Southwest Sciences, Inc., Santa Fe, NM) that is used to detect the methane emissions from landfills. This sensor is used in conjunction with **other** sensors providing local meteorological data to determine methane fluxes from the landfill areas.



## Conclusions

The use of tunable infrared lasers in environmental monitoring is currently benefiting from the coupled developments of robust laser sources with the required spectral properties and sophisticated instruments both for ground and airborne **use to** address atmospheric science questions and **global** environmental concerns. The development particularly of compact airborne laser sensing instruments capable of autonomous operation **reflects** engineering progress which can be utilized in other applications. To date **lidar** or other types of laser remote sensing technologies have found limited use in the areas of local pollutant measurement or industrial process control, primarily due to (1) the relatively high cost of the optical/laser instruments, (2) lack of suitable tunable laser sources in the important IR spectral regions, and (3) lack of low-cost spectral database and computational tools required for analysis of background spectra relevant to instrument calibration and measurement. Item (1) depends on the market economics once the suitable technology has been demonstrated in the innovative research environment. Item (3) has been addressed with new PC-level databases and software tools. **To** address item (2) the developing laser technology must include characteristics such as compactness, reliability, and minimum need for consumables along with the desired spectral characteristics. Recent developments indicate that the tools exist to meet these requirements during the next decade.

### Recommended Reading

**Two** excellent texts on use of tunable laser **techniques** for atmospheric chemistry studies and environmental monitoring are:

R.M. Measures, editor, Laser Remote Chemical Analysis, (J. Wiley, N.Y., 1988); and

E.D. Hinkley, editor, Laser Monitoring of the Atmosphere, (Springer-Verlag, N.Y., 1976).

The latter text, although written more than 15 years ago, treats the fundamentals of atmospheric transmission, **lidar** principles, TDL usage for detection of molecular pollutants, and laser heterodyne detection for both passive and active gas detection. The text edited by Measures provides valuable updated and expanded material, with additional applications based on technology developments.

Several excellent review papers exist in the technical journals, including the following:

W. Grant, R. **Kagann**, and W. **McClenny**, "Optical Remote Measurement of Toxic **Gases**", J. Air and Waste Management Assoc. **42**, 18-30 (1992) .

P.F. Moulton, "Pumping with Diodes", IEEE Circuits and Devices **7**, 36-40 (1991).

R.L. Byer, "Diode Laser-Pumped Solid-State **Lasers**", Science **239**, 742-747 (1988).

D.K. Killinger and N. Menyuk, "**Laser** Remote Sensing of the Atmosphere", Science **234**, 37-42 (1987).

W.B. Grant and R.T. Menzies, "A Survey of Laser and Selected Optical Systems for Remote Measurement of Pollutant Gas Concentrations" APCA Journal **33**, 187-194 (1983).

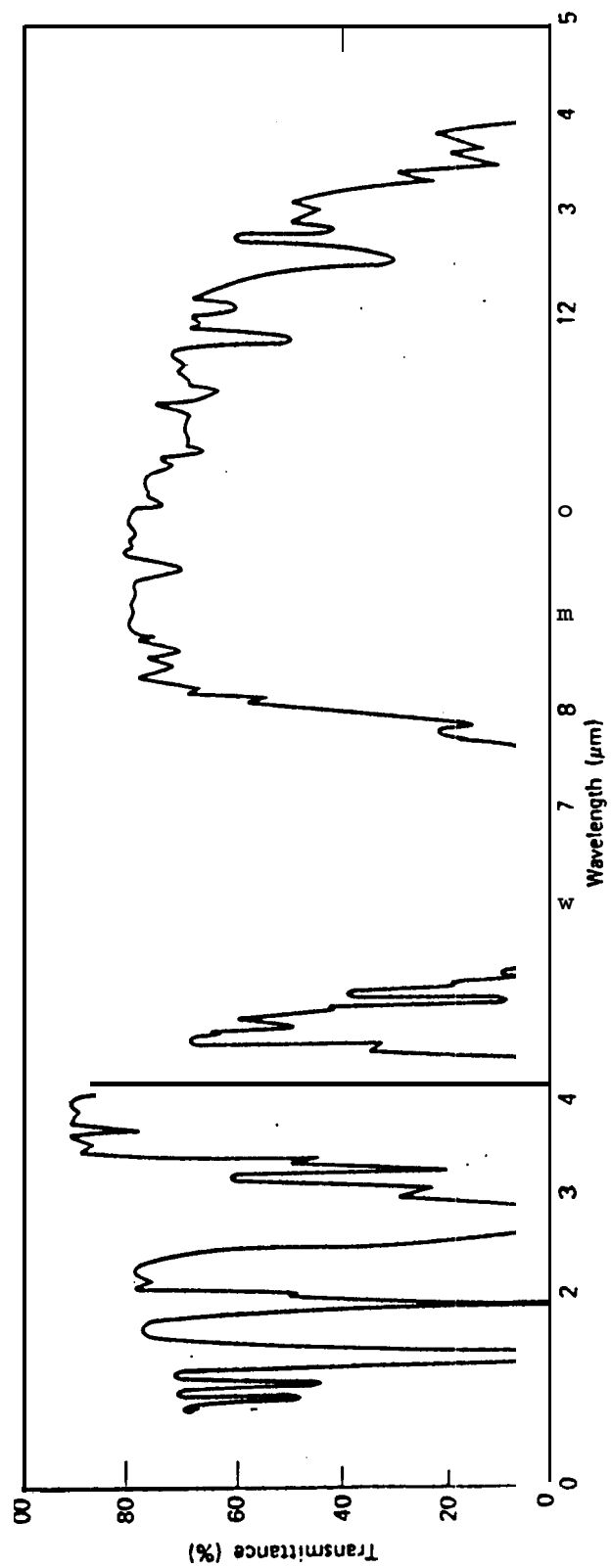
Specific citations to recent papers on the ALIAS and LASE instruments are:

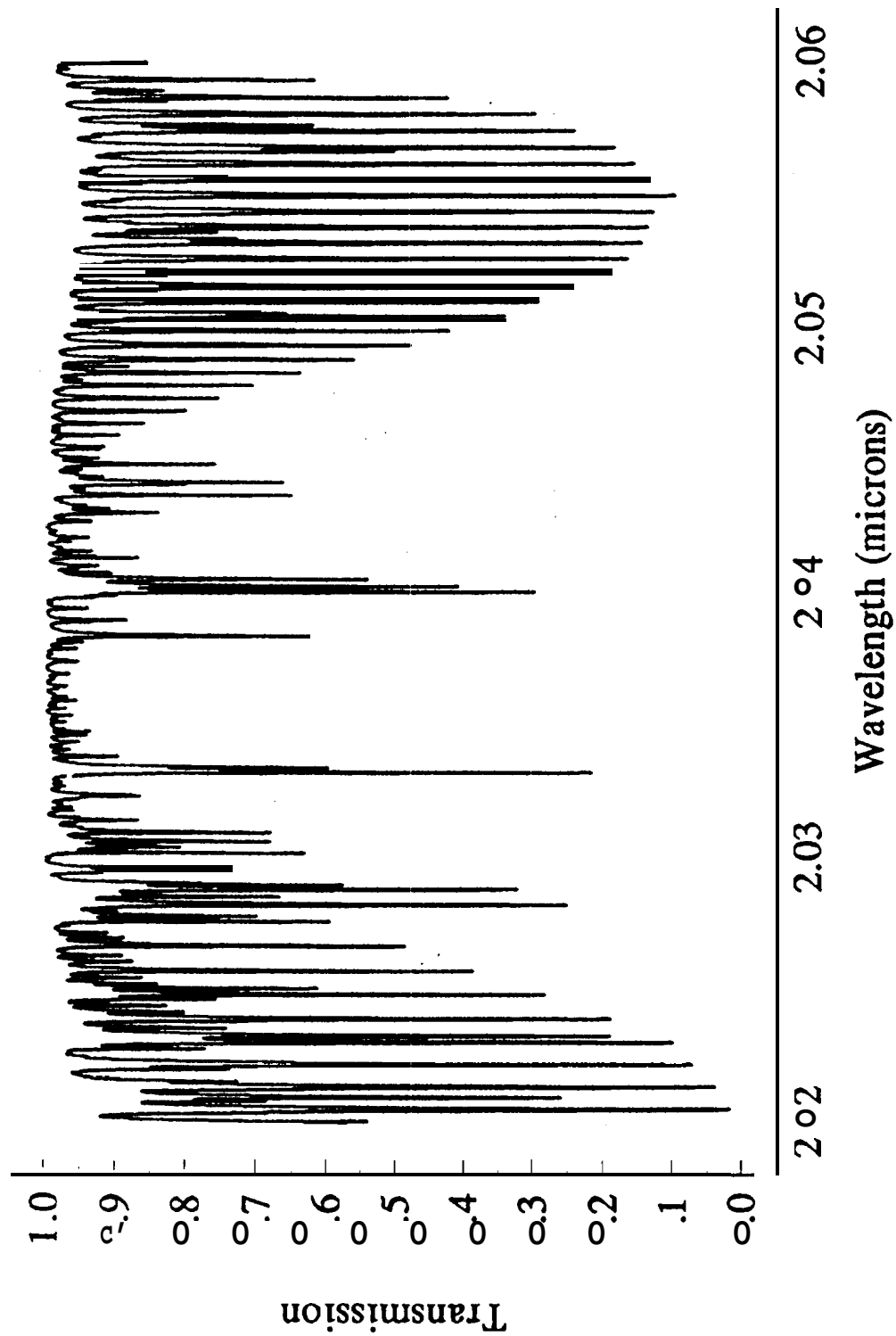
C.R. Webster, et al., "<sup>i</sup>Chlorine Chemistry on Polar Stratospheric Cloud Particles in the Arctic **Winter**", Science **261**, 1130-1134 (1993) ,

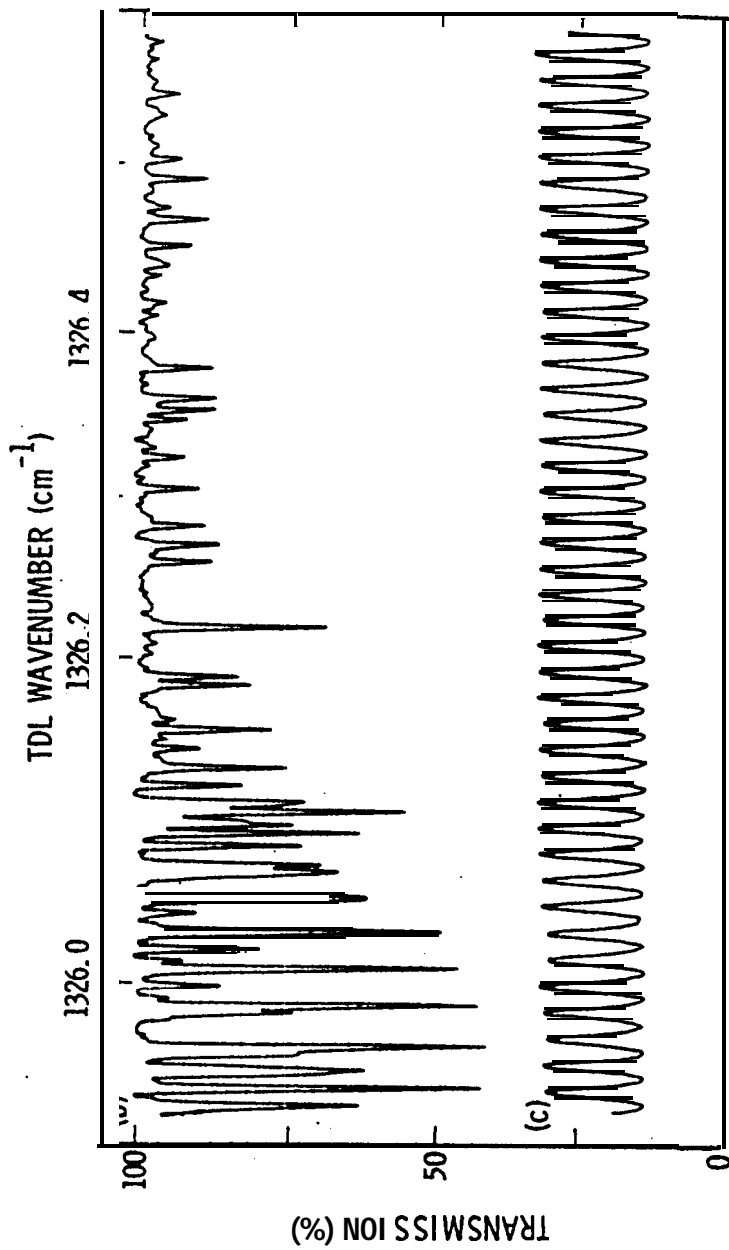
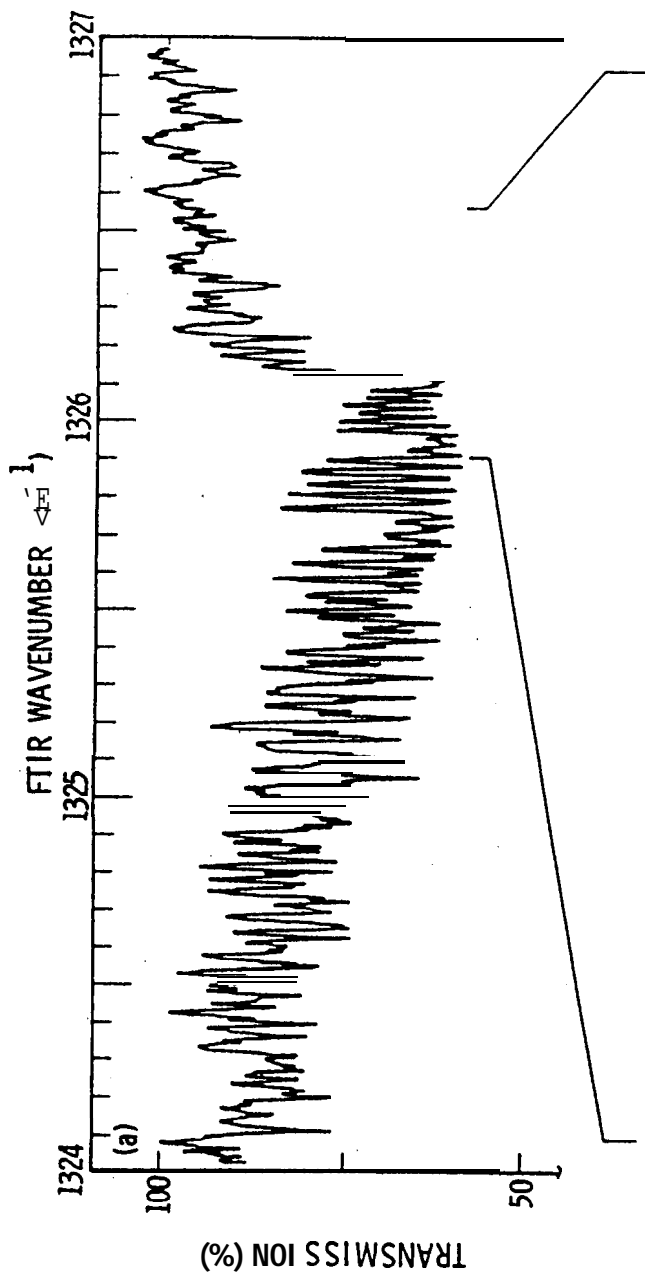
W.R. Vaughan and E.V. Browell, "A Lidar Instrument to Measure H<sub>2</sub>O and Aerosol Profiles from the NASA ER-2 Aircraft\*", presented at the Specialty Meeting on Airborne Radars and **Lidars**, Toulouse, France, July 7-10, 1992. (The authors are at NASA Langley Research Center, Hampton, Virginia, 23665-5225. )

## FIGURE CAPTIONS

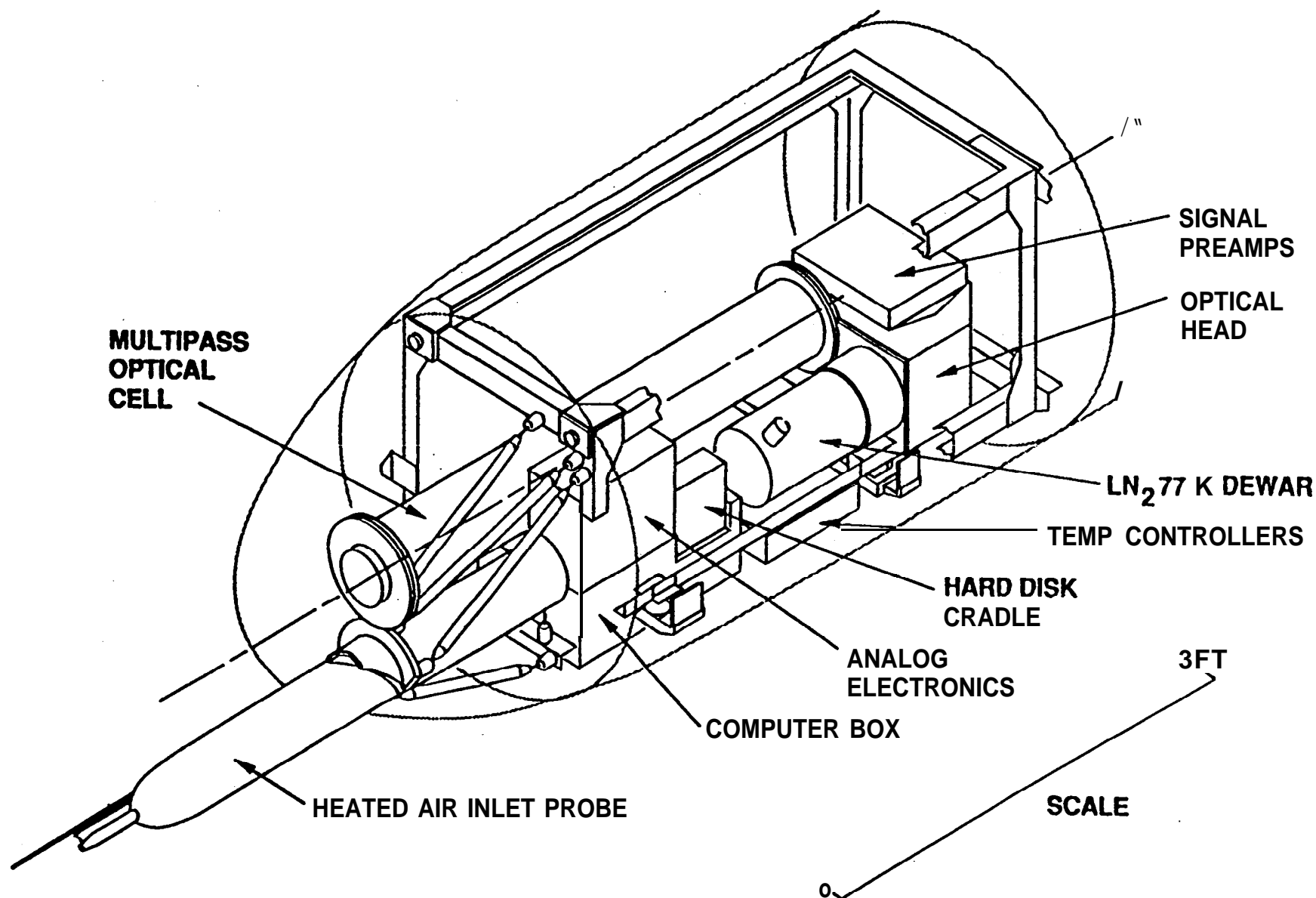
1. Broadband infrared spectrum of transmittance through the atmosphere along a horizontal path of 2 km.
2. Medium resolution spectrum of atmospheric transmittance near 2  $\mu\text{m}$ , also for a 2 km path at sea level, showing the structure of a  $\text{CO}_2$  band centered at 2.055- $\mu\text{m}$ .
3. Spectrum of nitric acid ( $\text{HNO}_3$ ) vapor in an absorption cell at low pressure, near a band origin at 1326  $\text{cm}^{-1}$ ; (a) taken with a high resolution FTIR instrument (0.005  $\text{cm}^{-1}$  resolution), and (b) taken with a tunable diode laser. A concurrent solid etalon fringe record (c) verifies continuous diode laser tuning through the scan. (This spectrum is described in C.R. Webster, R.D. May, and M.R. Gunson, *Chem. Phys Lett.*, vol. 121, pp. 429-436, 1985.)
4. Outline drawing of the Aircraft Laser **IR** Absorption Spectrometer (ALIAS) instrument, including the isokinetic sampling probe and other major components.
5. Block diagram of the Lidar Atmospheric Sensing Experiment (**LASE**) differential-absorption **lidar** instrument, showing the functional elements needed for water vapor profiling.
6. Schematic diagram of a fast-response sensor using a **near-IR** diode laser, to determine methane emissions at a landfill.







# AIRCRAFT LASER INFRARED ABSORPTION SPECTROMETER (ALIAS)





# LASE SYSTEM BLOCK DIAGRAM

